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Andrew J. Guenthner, Kevin R. Lamison, Josiah T. Reams, Vandana Vij, and

Joseph M. Mabry

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AFRL/RZS
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EFFECTS OF SILICON SUBSTITUTION IN THE MAIN CHAIN NETWORK SEGMENTS OF POLYCYANURATES

Andrew J. Guenthner,[1] Kevin R. Lamison,[2] Josiah T. Reams,[3] Vandana Vij,[2] and Joseph M. Mabry[1]

[1]Propulsion Directorate, Air Force Research Laboratory
Edwards AFB, CA 93524
[2]ERC Incorporated
Edwards AFB, CA 93524
[3]National Research Council / Air Force Research Laboratory
Edwards AFB, CA 93524

Abstract

The incorporation of silicon into thermosetting polymers at the molecular level has been shown to have several significant effects, beyond improving thermo-oxidative stability, as demonstrated by studies of silicon-containing cyanate ester resins. These effects are generally traceable to the enhanced flexibility afforded by the substitution of C-Si for C-C bonds, and include increased free volume and thermal expansion. In cyanate esters, the increased specific volume leads to a decrease in cyanurate ring density, which may explain the reduced water uptake in silicon-containing cyanate esters at high conversions. In addition, the increased flexibility provides for a greater degree of cure at lower temperatures than would otherwise be possible, leading, counter-intuitively, to a higher glass transition temperature for a given cure schedule. Due to the molecular level mechanisms involved, many of these effects are expected to be present in other silicon-containing thermosetting resins as well.

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Edwards AFB, CA 93524
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Edwards AFB, CA 93524

Introduction

The incorporation of silicon into otherwise organic polymer materials has long been recognized as an important means of achieving improved thermo-oxidative stability, whether in the form of particulate silica or clay fillers, sol-gel systems, silicate nanostrcutures such as polyhedral oligomeric silsesquioxane,[1] or even via replacement of single carbon atoms for silicon atoms in the chemical repeat unit. For thermosetting polymers, the latter approach is typically the most effective at maintaining ease of processing, since the silicon is covalently bound to the polymer and since the size and shape of repeat units is altered only modestly. Indeed, examples of silicon substitution at the molecular level can be found for epoxy resins,[2-5] cyanate ester resins,[6-8] maleimide resins,[9] and benzoxazine resins.[10] Of these, the silicon-substituted cyanate ester resin has proven to be particularly useful in understanding structure-processing-property relationships for thermosetting resins, in part because the high selectivity of the cyanate ester cure reaction,[11] along with the ease of identifying common side products via infrared spectroscopy,[12] allows the chemical structure of even the insoluble polycyanurate network to be verified with a relatively high level of precision and reliability for a thermosetting polymer. In what follows, many of the remarkable effects, beyond improvements in thermo-oxidative stability, of even a small level of silicon substitution at the molecular level in the main chains of polycyanurate networks are described, based on work carried out over the past few years on a single silicon-containing cyanate ester compound (shown in **Figure 1**), referred to herein as "SiMCy".

Experimental

Materials. Bis(4-cyanatophenyl)dimethylsilane, or "SiMCy" was first prepared by Dr. Michael Wright at the Naval Air Warfare Center, Weapons Division (NAWCWD) China Lake and reported in 2004.[6] The synthesis and physical properties of the compound were reported in more detail by Guenthner et al.[7], with additional physical data having been reported more recently[13-15] in connection with studies of polymer blends. Samples of SiMCy were synthesized in our laboratory following the published procedure.[7] Samples of 2,2'-bis(4-cyanato)propane ("BADCy") and 1,1'-bis(4-cyanato) ethane ("LECy") were obtained from Lonza and used as-received for comparison purposes. Nonylphenol (technical grade) was purchased from Aldrich, and copper (II) acetylacetonate was purchased from ROC/RIC; all were used as received.

Sample Preparation. Batches of catalyst comprised of 30 parts by weight nonylphenol to one part by weight of copper (II) acetylacetonate were prepared by mixing the ingredients in a vial and heating to 60 °C while stirring vigorously until complete dissolution took place (typically one to two hours). Silicone molds (R2364A, Silpak Inc., mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour) were prepared by de-gassing for 60 minutes at 95 °C and 300 mm Hg. Cyanate ester monomers were mixed with 2 phr catalyst and de-gassed for 30 minutes at 95 °C and 300 mm Hg, then poured into the prepared mold. The open mold and sample were then placed under flowing nitrogen and cured. Cure schedules were varied so as to achieve conversions of 70 – 100%, with the final step taking place at no more than 210 °C. All curing operations took place under nitrogen, and all schedules produced void-free samples 1-3 mm thick. The temperature ramp rate during cure was 5 °C/min.

Test Procedures. Density was determined by placing selected samples in aqueous solutions of CaCl₂ (added as the dihydrate) and varying the CaCl₂ concentration until neutral buoyancy was observed on bubble-free samples over a period of several minutes. The density of the neutrally buoyant
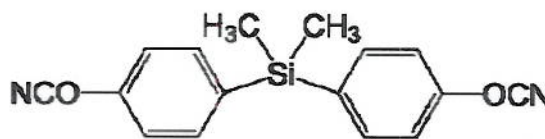

Figure 1. Chemical structure of "SiMCy"

solution was determined by placing 10.00 mL in a volumetric flask (calibrated with deionized water at 20 °C) and weighing, and checked against the predicted density of the solution at ambient temperature based on the known concentration of CaCl₂. Water uptake was determined by placing unused samples in approximately 300 mL of deionized water at 85 °C for 96 hours, with sample dimensions and weight measured before and after exposure.

Dynamic thermomechanical analysis was performed under oscillatory compression to determine the glass transition temperatures of samples before and after exposure to boiling water. The dynamic TMA technique is similar to traditional DMTA, but provides only a relative measure of stiffness as opposed to an absolute modulus. A detailed description of the dynamic TMA experiments is provided elsewhere.[13] Heating rates were 20 °C/min for all samples. Differential scanning calorimetry was conducted using a TA Instruments Q2000 calorimeter, with heating to 350 °C followed by cooling and re-heating, to determine the extent of conversion, at a ramp rate of 10 °C / min.

Results and Discussion

Figure 2 compares the density of BADCy, LECy, and SiMCy as a function of conversion (as determined by DSC). All three materials follow a similar trend, with the data for BADCy closely resembling the published results of Georjon and Galy.[16] In all cases, the post-gel stage of resin cure induced a net increase in free volume at room temperature. The packing fraction of SiMCy at room temperature, however, is lower (at about 0.62) than either BADCy or LECy (at 0.63).[14] The coefficient of thermal expansion for SiMCy, however, is significantly higher than for BADCy or LECy,[13] thus at very low temperatures the packing fractions are similar. It thus appears that the relatively flexible C-Si bonds found in SiMCy facilitate thermal motion of the network segments, allowing for greater free volume at elevated temperatures. This effect should result in a modestly lower elastic modulus in the glassy state, as observed, and should also enhance toughness, though measurements to date (in which the degree of cure was not precisely controlled) show little difference.[7] These features associated with the molecular level substitution of silicon are likely to be replicated in most other thermosetting networks

Based on the foregoing discussion, it might appear that by creating additional free volume, the incorporation of silicon into thermosetting networks would result in increased moisture uptake. However, as **Figure 3** shows, in the case of cyanate esters, although moisture uptake increases drastically at lower conversions (where the glass transition temperature, which is initially somewhat lower for a given conversion in SiMCy, is brought closer to the exposure temperature by plasticization, thereby inducing network degradation and more plasticization in a vicious cycle), at higher conversions moisture uptake is in fact significantly lower for SiMCy, despite the fact that the packing fraction is lower. It appears that moisture uptake in cyanate esters is sensitive not simply to free volume, but to free volume in the vicinity of (likely multiple) cyanurate rings, being highly sensitive to cyanurate ring density.[15] The lower density in SiMCy thus results in a cyanurate ring density which is about 10% lower than in BADCy or LECy, which is sufficient to provide significantly less water uptake. The extent to which this trait appears in other thermosetting resin systems will depend on the specific mechanisms of water absorption.

Although for a given conversion, the dry glass transition temperature of SiMCy is somewhat lower than for BADCy or LECy due to the incorporation of flexible C-Si bonds, for a given cure schedule, SiMCy can achieve a higher glass transition temperature, as seen in **Figure 4**. The data presented are for samples cured for 12 hours at the indicated temperature, with the sample cured at 200 °C also subjected to one hour of heating at 150 °C to prevent excess volatilization.
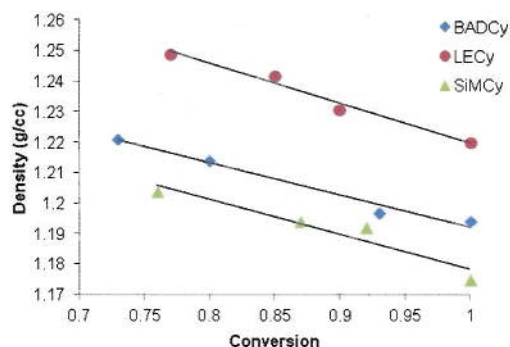
Figure 2. Density of cyanate ester resins as a function of conversion
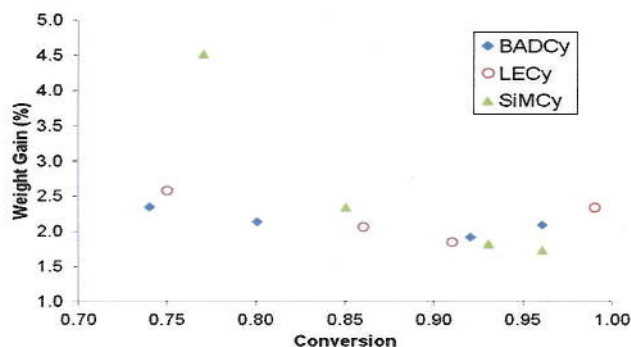

Figure 3. Weight gain after exposure to water at 85 °C for 96 hours as a function of conversion. Data at full conversion was derived from a regression of blend data for 16 samples incorporating effects of composition and cure.
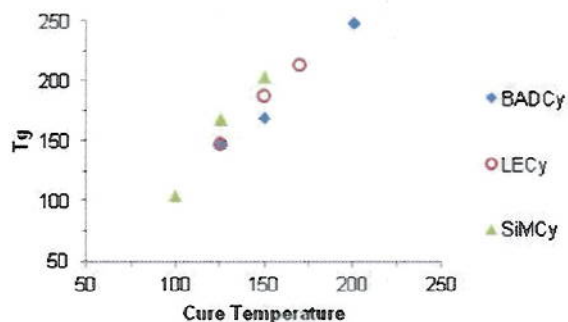

Figure 4. Dry glass transition temperature as a function of maximum cure temperature.

As expected, there is a close relationship between the maximum cure temperature and the consequent dry glass transition temperature. In cyanate esters, however, as careful inspection of **Figure 4** shows, the dry glass transition temperature tends to be somewhat higher than the final cure temperature due to the slow continuation of cure even in the glassy state. Under such circumstances, the flexible C-Si bonds placed at the core of the monomer appear to enable SiMCy network segments to adopt a wider range of physical configurations, which in turn enables the uncured end groups to adopt an appropriate arrangement for cyclotrimerization more readily. Thus, counter-intuitively, the flexibility of the C-Si bonds enables a higher dry glass transition temperature by enabling the resin to reach a higher degree of cure at a given cure temperature. Note that a similar effect of flexibility has been observed for uncatalyzed tricyanate esters as well.[17] In fact, this effect should be present in any thermosetting polymer capable of undergoing significant cure at temperatures slightly below the glass transition temperature.

Conclusions

The incorporation of silicon into thermosetting polymers at the molecular level has been shown to have several significant effects, beyond improving thermo-oxidative stability, as demonstrated by studies of silicon-containing cyanate ester resins. These effects are generally traceable to the enhanced flexibility afforded by the substitution of C-Si for C-C bonds, and include increased free volume and thermal expansion. In cyanate esters, the increased specific volume leads to a decrease in cyanurate ring density, which may explain the reduced water uptake in silicon-containing cyanate esters at high conversions due to the known correlation between water uptake and cyanurate density. In addition, the increased flexibility provides for a greater degree of cure at lower temperatures than would otherwise be possible, leading, counter-intuitively, to a higher glass transition temperature for a given cure schedule, even though, for a given degree of conversion, the dry glass transition temperature of the more flexible network is, as expected, somewhat lower. Due to the molecular level mechanisms involved, many of these effects are expected to be present in other silicon-containing thermosetting resins as well.

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